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Three years of working experience with different solvents at a realistic post combustion capture pilot plant

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Abstract

A test facility for the investigation of the CO_2 post combustion process named CO_2SEPPL (acronym for CO_2 SEParation Plant) was erected in 2010 by EVN and ANDRITZ Energy & Environment at the EVN power plant station in Dürnrohr (Austria). Since the test facility has an absorber height on an industrial scale and operates with flue gas of a natural gas- or coal-fired boiler, realistic results can be achieved. The pilot plant is designed for a flue gas flow rate of 100 m^3/h_{STP}. The test facility allows a variation of many operating parameters. A sensitivity analysis was carried out for each solvent. In addition to the standard solvent 30 wt% monoethanolamine (MEA), other aqueous solvents were investigated. Separation using aqueous solutions of the amines piperazine (PZ) and ethylenediamine (EDA) enables significant energy savings compared to 30 wt% MEA. In order to reduce emissions of harmful substances, absorbents with very low or non-existent vapor pressure were tested (sodium glycinate). These investigated solvents have a high energy demand because of poor mass transfer and slow kinetics. Experimental results are explained on the basis of physical/chemical solvent data and technical specifications of the pilot plant.

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Keywords: CO_2 post combustion capture; pilot plant studies; monoethanolamine; piperazine; ethylnediamine; potassium carbonate; amino acid salts

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1. Introduction

Post combustion capture (PCC) enables the reduction of CO_2 emissions from flue gases. Compared to other technologies (e.g. Oxyfuel process, IGCC …), this process affects the operation of the power plant only slightly. At low partial CO_2 pressures, aqueous amines are the most suitable solvents for the absorption and desorption process [1]. An aqueous solution of 30 wt% monoethanolamine (MEA) has become established as standard solvent. Extensions of the basic PCC process such as vapor re-compression and absorber intercooling enable a decrease in energy requirement. However, the capital outlay and operating costs of PCC are still high. In order to make PCC economically competitive, it is important to reduce the operating and investment costs.

The operating costs can be reduced primarily through a reduction in energy requirement for solvent regeneration. The location of the optimum operating point is critical, too. Small solvent flow rates are advantageous because less solvent has to be heated in the desorber. Furthermore, the energy requirement for pumping is reduced. The total piping can be made smaller. This in turn leads to a reduction of the investment costs. In addition, less heat has to be dissipated in the heat exchangers. The quantity of the dissipated heat is often a determining factor for the design of power plants. A lower optimal operating pressure of the desorber allows the reduction of exergy loss in the power plant process. A further reduction of investment costs can be achieved through a smaller dimensioning of the absorber column. Fast kinetics and good mass transfer properties of the solvents are advantageous for reaching equilibrium CO_2 loading of the CO_2-enriched solvent.

Degradation of solvents results in a loss of active absorbent. The loss of solvent has to be compensated by the addition of fresh absorbent. Therefore, the price of the solvent is not only reflected in the investment but also in the operating costs. Volatile solvents and solvents which form volatile degradation products can lead to harmful emissions, resulting in additional investment costs for a downstream flue gas cleaning line. A low corrosivity of solvent allows a significant cost reduction.

The aspects mentioned above can be studied in the pilot plant. Various solvents were investigated in the last three years of operation. The pilot plant enables the realistic investigation of a solvent within a short time. This is achieved by the small filling volume of 120 liters, resulting in short circulation times. Thus, a stable measurement point can be achieved within a short time.

With the standard solvent 30 wt% MEA, the specific regeneration energy could be reduced by the optimum setting of operating parameters up to 3.5 GJ per ton of separated CO_2 (GJ/t_{CO2}). In addition to the relatively high energy requirement, MEA is corrosive and degrades under the influence of O_2, NOx, SO_2 and heat. The objective is to find a solvent which is more energy-efficient as well as stable against degradation. Moreover, the operating safety must be ensured.

2. CO_2 post combustion pilot plant CO_2SEPPL

The measurements were performed at a pilot plant at the EVN power plant in Dürnrohr, Austria. The post combustion capture test facility, known as CO_2SEPPL (CO_2 SEParation PLant), was Austria's first carbon dioxide removal plant for flue gases originating from the thermal conversion of fossil fuels. The power plant is powered by hard coal. Short-term experiments with flue gases from a natural gas-fired boiler can be carried out as well. Fig. 1 shows the flow scheme of the pilot plant. In addition to the capture part, the test rig is equipped with a CO_2 compression unit (not depicted) in order to demonstrate the compression link in the CCS chain as well.

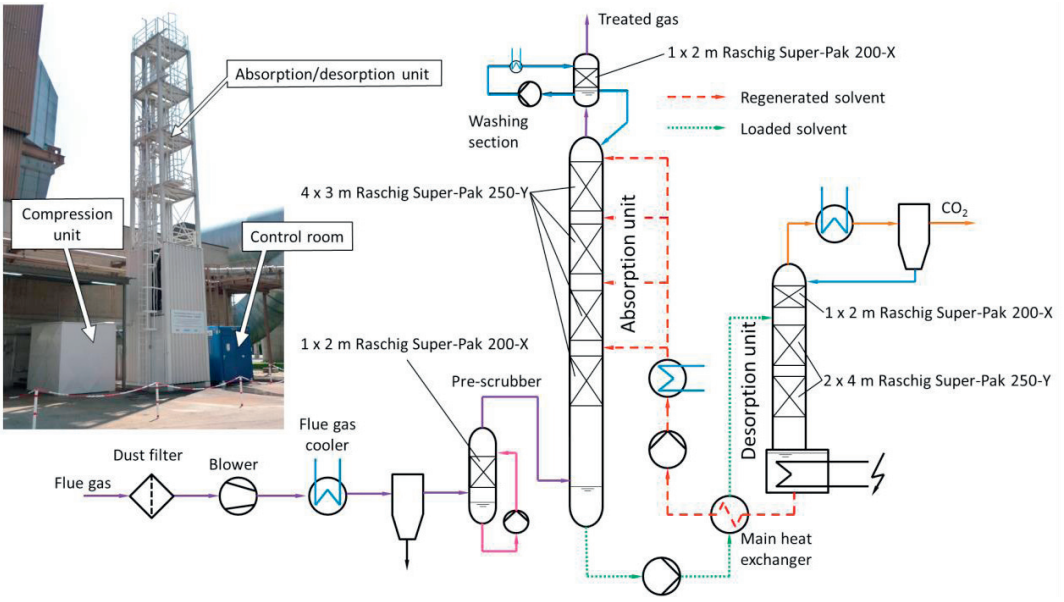

Fig. 1. Flow diagram of the pilot plant

A slipstream of the flue gas is branched off to the pilot plant downstream to the flue gas cleaning line and the draught fan of the power plant. The flue gas passes through a dust filter. A downstream blower increases the pressure and enables flue gas flow rates up to 100 m^3/h_{STP}. This corresponds to an F-factor of about 2 $Pa^{0.5}$ in the absorber column. Through a heat exchanger, which is connected downstream of the blower, the temperature of the flue gas at the absorber entry can be set. The pre-washer column reduces the content of sulfur oxides, which otherwise would lead to higher degradation rates of the chemical absorbent. The lean solvent is fed to the absorber top. Both, the absorber and the desorber are equipped with a demister unit. In order to maintain the water balance for the entire system, there is a water washing section located at the top of the absorber above the solvent inlet, which additionally reduces various degradation products in the treated gas. The CO_2-enriched solvent is pumped into the desorber via the main heat exchanger. The solvent is heated by an electrical heating rod in the desorber sump which produces the stripping steam. The vapor exiting the desorption unit contains water, CO_2 and some traces of other volatile components. In order to reduce the emissions, a washing section is also installed at the top of the desorber. In contrast to the absorber washing section, the washing water is not pumped in a circuit, but provided by a downstream condenser. The total water balance is closed by recirculating condensate.

The whole test facility is equipped with a sophisticated measuring system. For example, there are thirteen temperature sensors installed along the absorber column. The lowest sensor is located in the sump of the absorber and measures the temperature of the loaded solvent. The other sensors measure the resulting temperature of the liquid and gaseous phase, thus allowing a high resolution temperature curve to be produced. Furthermore, the pressure loss of the flue gas flow is monitored along the entire flow path. System control through a PCS (process control system) allows comprehensive control concepts.

3. Investigated solvents

In addition to the standard solvent 30 wt% MEA, the following aqueous solvents, inter alia, were tested in the last three years of operation in the pilot plant.

- 25 and 37.6 wt% piperazine (PZ)
- 22.1 wt% potassium carbonate promoted with 11.1 wt% piperazine (K_2CO_3/PZ)
- 32 wt% ethylenediamine (EDA)
- 15, 25 and 40 wt% sodium glycinate (NaGly)

3.1. Piperazine (PZ)

PZ is a heterocyclic amine and can be used in a concentrated form or as an additive to other solvents. Compared to MEA, PZ has nearly double the loading capacity of CO_2 at double the reaction rate [2]. The heat of absorption of PZ is similar to that of MEA [3]. Thermal and oxidative degradation are lower than those of MEA [2]. Although, pure PZ has a lower boiling point than pure MEA, it is less volatile due to its low activity coefficient in water [4].

3.2. Potassium carbonate promoted by piperazine (K_2CO_3/PZ)

As opposed to amine solutions, K_2CO_3 has a low heat of absorption. Due to the very low absorption rate of K_2CO_3, this solvent cannot be used without other solvents. Because of its fast kinetics, PZ can be used as promoter.

3.3. Ethylenediamine (EDA)

EDA is a primary diamine and can thus bind twice as much CO_2 per molecule as MEA. EDA has a similar absorption heat as MEA [5]. EDA has fast kinetics and high CO_2 absorption capacities, determined by laboratory tests.

3.4. Sodium glycinate (NaGly)

Glycine is the simplest primary amino acid. When the acid group is titrated with a base (e.g. sodium hydroxide) an amino acid salt is formed [6]. The advantage of amino acid salts is that they have a non-existing vapor pressure. Thermal degradation of NaGly is higher than that of MEA [7]. Through degradation, products with measurable vapor pressure can be formed, leading to higher emissions.

4. Results and Discussion

The default process parameters are listed in Table 1. The CO_2 flue gas content varied between 11 and 13 vol% (dry) during the tests and depends on the power plant operation. Studies with flue gas from a natural gas-fired boiler are not described in this research work. The flue gas flow rates are not set optimally for each solvent. For example, a series of experiments by Posch (2012) [8] were carried out before the installation of a larger-sized flue gas blower and were therefore limited to 70 m³/h. Since this conversion, flue gas flow rates up to 120 m³/h (100 m^3/h_{STP}) have been possible. In the experiments with NaGly, there was a limitation of the flue gas flow rate at 50 m³/h because of the required solvent flow rate.

Table 1. Default process parameters.

	30 wt% MEA	25 wt% PZ [8]	37.6 wt% PZ	22.1 wt% K_2CO_3 / 11.4 wt% PZ [8]	32 wt% EDA [9]	15 wt% NaGly	25 wt% NaGly	40 wt% NaGly
Flue gas flow [m³/h]	90	70	100	70	90	50		
Separation efficiency [%]	90 ± 1							
Absorber height [m]	12							
Temperature of the regenerated solvent [°C]	40							
Temperature of the flue gas [°C]	40							
Desorber pressure [bar_{abs}]	2							

4.1. Minimal energy for solvent regeneration

Fig. 2a shows the specific energy for solvent regeneration of the investigated solvents as a function of the L/G-ratio (liquid to gas ratio). The minimum energy consumption of the standard solvent, 30 wt% MEA is 3.67 GJ/t_{CO2}. The optimal L/G-ratio is 3.2 l/m³. 30 wt% MEA measurement results of other, sometimes much larger pilot plants are similarly with results determined in Dürnrohr. The energy consumption of 37.6 wt% PZ and 32 wt% EDA is significantly lower than that of 30 wt% MEA. The optimal L/G-ratio of these solvents is located advantageously. Only 80 % of the volume flow of 30 wt% MEA needs to be circulated to reach the optimal operating point. K_2CO_3 promoted with PZ shows no benefits compared to 30 wt% MEA.

The investigated aqueous solutions of NaGly have energetic disadvantages as compared with the amine solutions or amine-promoted solutions. The minimum energy requirement increases to 5.4 GJ/t_{CO2}. An equilibrium CO_2 loading of the CO_2-enriched solvent in the test facility is not possible due to the slow kinetics. The low CO_2 partial pressures required in the desorber top lead to enormous amount of stripping steam to be generated. In addition, the required solvent stream is very high when using aqueous NaGly solutions.

Fig. 2b shows the absorber temperature profile of different solvents at the optimal operating point. The absorber temperature profiles of 30 wt% MEA, 37.6 wt% PZ and 32 wt% EDA are nearly congruent because of similar absorption enthalpies and process parameters. The temperature maximum for the investigated amine solutions is directly below the lean solvent inlet and amounts to 72 - 75 °C. When using 25 wt% NaGly, the temperature maximum is located at a lower position of the column, reflecting a suboptimal L/G-ratio. By using 40 wt% NaGly as solvent, no typical temperature could be formed. The temperature in the lower part of the absorber is higher when using NaGly than when using the investigated amines. The higher temperature increases the kinetics. However, the higher temperature decreases the CO_2 equilibrium loading. By using the investigated amine solutions, the contact time of gaseous and liquid phase is sufficient to almost reach equilibrium loading. When using NaGly solutions, the theoretical number of separation plates should be increased in order to achieve equilibrium loading, too. In the following, the performance of the most promising solutions (30 wt% MEA, 37.6 wt% PZ and 32 wt% EDA) should be explained in more detail.

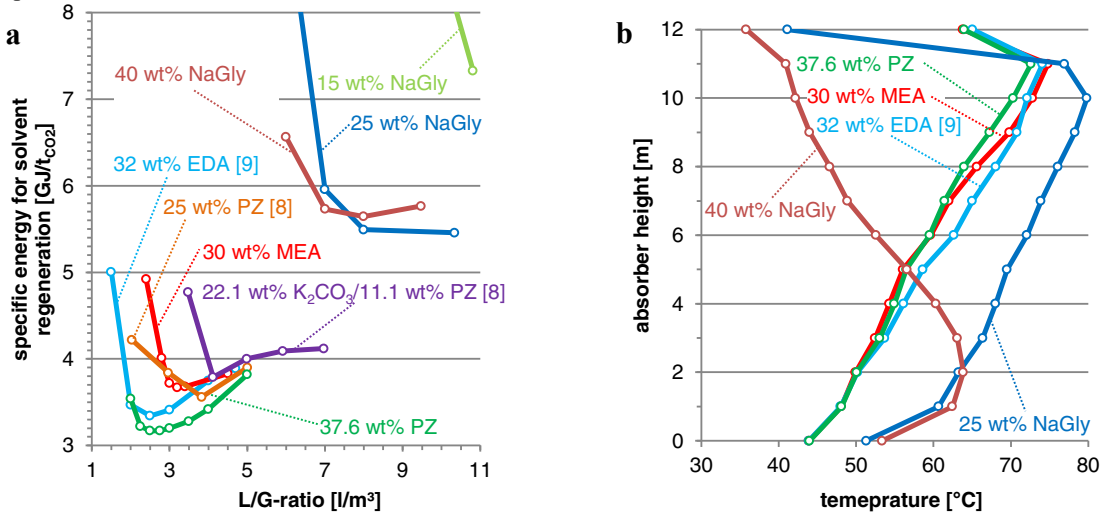

Fig. 2. (a) Specific energy for solvent regeneration as a function of the L/G-ratio; (b) Absorber temperature profile at the optimal operating point.

4.2. Influence of different operating parameters

When the flue gas flow rate is increased, 30 wt% MEA, 37.6 wt% PZ and 32 wt% EDA brings about a lowering in energy demand (Fig. 3a). In Fig. 3 and 4 the optimal L/G-ratio determined by Fig. 2a was set. When using 37.6 wt% PZ, the energy consumption can be reduced to 3 GJ/t_{CO2}. The considered solvents have a similar desorber sump temperature at the same desorber pressure (Fig. 3b). However, by using 30 wt% MEA there is a huge increase in energy demand at pressures below 2 bar_{abs}. For 32 wt% EDA and 37.6 wt% PZ, this increase is not so significant. These solvents enable desorber operation with lower pressure steam and, as a consequence, lead to a lower exergy loss from the power plant.

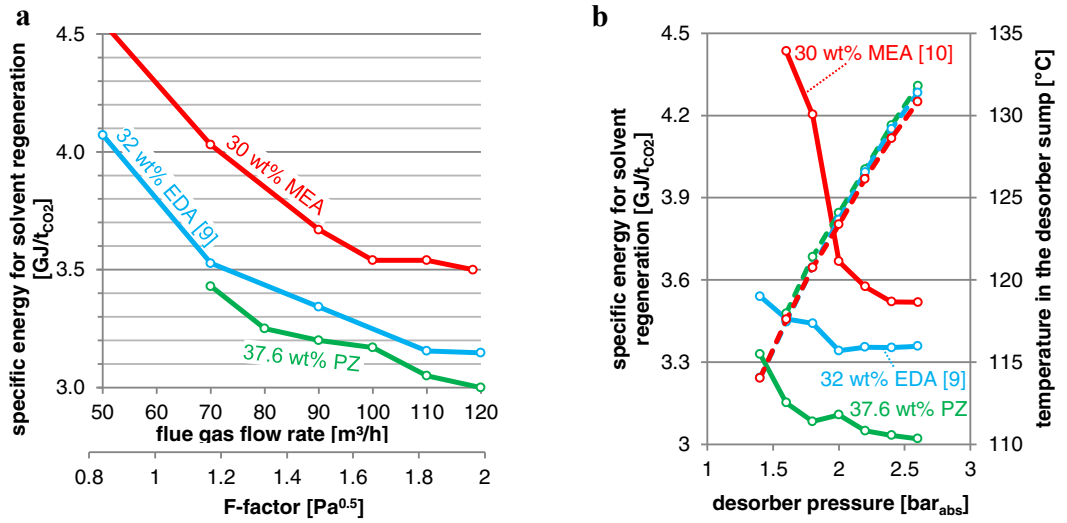

Fig. 3. (a) Specific energy for solvent regeneration as a function of the flue gas flow rate; (b) Specific energy for solvent regeneration (—) and temperature in the desorber sump (- -) for different pressures.

The effective absorber height of the test rig can be varied between 3, 6, 9 and 12 m by manually opening and closing of ball valves. At an absorber height of 3 m, stationary operation conditions are hard to achieve since 90 % absorption efficiency should be achieved. Fig. 4 shows the specific energy for solvent regeneration at different absorber heights. PZ with the fastest absorption rates shows the smallest increase of the energy requirement for a decreasing absorber height.

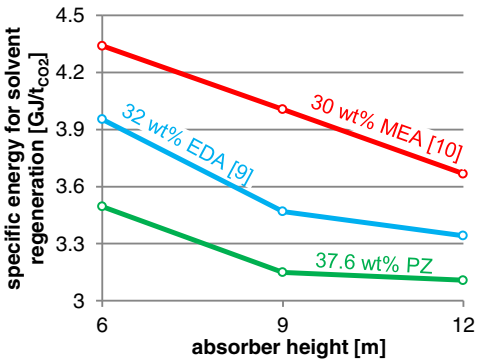

Fig. 4. Specific energy for solvent regeneration as a function of the total absorber height.

5. Outlook

The investigations on the CO_2SEPPL pilot plant show that there are promising alternative solvents to the standard solvent MEA. The aqueous amine solutions 37.6 wt% PZ and 32 wt% EDA in particular have a lower energy requirement. Both solvents require a low solvent flow to reach the optimal operating point. With decreasing desorber pressure, these solvents still have an energy demand lower than that of 30 wt% MEA at 2 bar_{abs}. This enables the minimizing of exergy loss of the power plant by the diversion of steam. The fast absorption rates of PZ allow equilibrium loading to be reached despite lower absorber columns, thus resulting in lower investment costs. Foaming of PZ can already be prevented by adding small amounts of a defoamer. The high melting point of PZ can lead to problems during a system failure, but this issue can be eased by loading with CO_2 for lowering the melting point. Critical parts of the plant have to be trace-heated if a certain CO_2 loading cannot be guaranteed. EDA has proven to be easy to handle.

In the future, more alternative solvents will be examined for suitability. The focus will be on solvents with low vapor pressure. The main objective of the upcoming project is to investigate the emissions of the treated flue gas exiting the absorber. For this purpose, the exhaust gas will be studied for specific degradation products using gas chromatographic analysis.

Acknowledgements

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